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DISPOSAL AND RECOVERY OF 49
CLINTON LABORATORIES
WASTE DISPOSAL
DECEMBER 4. 1943

For N. T. Bay, Supervisor

I. Introduction and Summary.

The Clinton waste disposal system was designed for the wet fluoride process. At the present, emphasis is placed on the bismuth phosphate process although it is expected that both processes will be run. Hence both fluoride and phosphate wastes will have to be taken care of with the existing facilities, which consist of (see Figure I):
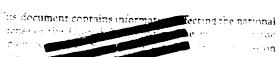
A. Three pairs of underground concrete tanks, each of 176,500 gallon capacity;

B. Two 44,000 gallon underground concrete tanks;

C. Three 5,000 gallon underground concrete tanks which may be emptied separately either into the 176,500 gallon storage tanks (A) or into the large ponds (E);

D. One 14,000 gallon buried concrete tank for the use of Building 706-A;

E. Two large (225,000 gallon) and one small retention ponds.

All waste solutions will be neutralized to a pH ≥ 8 with 30% sodium carbonate solution to minimize corrosion during transfer and storage. All metal-containing wastes will be segregated to facilitate eventual metal recovery. One pair of the 176,500 gallon tanks will be used to store this neutralized metal waste solution. These will provide storage for approximately two hundred days' operation (processing one-third ton of metal per day, in 20% UNH solution). Active non-metal wastes will be stored in the second and third pairs of large tanks. The first tank will fill up in about seventy-five days' operation ($BiPO_4$ process; greater than one year for wet fluoride) at which time the contents will be pumped to the second of this pair, where it will be allowed to decay while the first tank refills. When the first pair of tanks is full, this procedure is repeated on the second pair. As soon as one tank of the second pair is full, the longest stored tank full of waste is pumped into the river, with dilution water, at the same rate at which the empty tank is being filled. Thereafter, continuation of this cycle of emptying the longest stored tank full of waste while filling up the last empty tank will allow disposal of the decontamination wastes without additional tanks. With this decontamination storage cycle, the minimum hold-up of decontamination waste is ca. 225 days, during which time the activity will have decreased twenty-fold, therefore requiring at most 250 gallons per minute of dilution water for safe disposal into the river. It is believed that enough inactive process water will be available for this dilution.

Plant experience may show that the decontamination waste activity is low enough, or the amount of inactive dilution water high enough, to require

only two or three of the large tanks for safe operation of this decontamination waste hold-up and disposal process, in which case the extra one or two tanks can be used for metal-containing waste. This would increase the effective service life of the present metal waste solution storage tanks from two hundred days to three or four hundred days.

Inactive wastes such as plant process water, floor washings, etc. will be monitored and sent to the river via the larger retention ponds. This water (estimated flow - 200-500 gallons per minute) is available for dilution of active wastes before discarding into the river.

Slightly active wastes (concentration cycle) will be stored temporarily in two of the 5,000 gallon tanks. Here they will be monitored and, if the activity is low enough so that after mixing with the inactive wastes in the pond the resulting activity will not be greater than 2×10^{-11} watts/cc. (1×10^{-4} curies/cu.ft., or 0.1 r./24 hours' immersion), they will be pumped to the pond and thence to the river. Otherwise they will be included with the active non-metal wastes in the large storage tanks.

Metal wastes from 706-A will be stored in the 14,000 gallon tank, active non-metal wastes in the third of the 5,000 gallon tanks, from which they will be sent to active storage or to the river via the pond, depending on their activity.

All buried tanks are surrounded by a sump which may be reached for sampling by means of a concrete dry-well. Seepage which collects in these sumps drains to the third, smaller, retention basin, from which it may be sent to the river after monitoring.

No immediate use is planned for the two 44,000 gallon buried tanks. These remain available for emergency use, or for special storage problems.

II. **Types of Wastes**

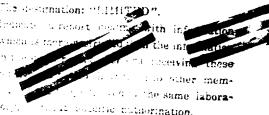For disposal purposes the wastes are divided into the following:

A. Aluminum coating solution,

B. Metal-containing solutions (extraction wastes),

C. By-product precipitate solutions or slurries,

D. Non-metal-containing decontamination solutions,

E. Slightly active concentration wastes,

F. Room D waste,

G. Inactive process water and floor washings.

III. Handling the Wastes

Although decreases in volumes of alkali and of stored neutralized wastes could be obtained by using part caustic and part sodium carbonate for neutralizing the wastes (see Appendix), it has been decided to use only one alkali in the waste disposal process, since the plant now has only one alkali solution tank and delivery line to the neutralizer. As it is desirable to handle only solutions or thin slurries which are easily pumped through pipe lines, sodium carbonate is used, because neutralization of the metal-containing solutions with caustic produces bulky insoluble precipitates, whereas the metal salts form a soluble, heat stable complex with excess carbonate. The by-products form a precipitate with excess carbonate but the amount of precipitate is small enough that the slurry is free flowing. In making the neutralization the waste is added to the carbonate solution to avoid excessive CO_2 evolution. Some CO_2 evolution is unavoidable since it is impossible to get complete and instantaneous mixing in the neutralization tank.

The 30% sodium carbonate solution should be kept at 35-40° C. to ensure that the carbonate remains in solution. Assuming that all solutions are neutralized at 35° C., the temperature of the neutralized slurry will not be more than 60° C., due to heat of neutralization.

A consideration of the handling of the separate waste solutions follows.

A. Aluminum Coating Solution

This solution, containing about 0.1% of the fission activity and of the metal, is neutralized and stored in the metal waste storage tanks (pair A of the 176,500 gallon tanks). About 200 gallons of neutralized coating solution in the form of a gelatinous slurry must be handled each day. This slurry flows freely and contains 7% dry solids when neutralized to a pH of 7-9. The solids therein are readily redispersed after settling, even by air agitation.

B. Metal Waste

In both the bismuth phosphate and wet fluoride processes the product will be separated first from the metal (extraction step) and then from the radioactive fission products (decontamination and concentration steps). For either process the waste solution from the extraction step, which contains essentially all of the metal, is neutralized with 30% sodium carbonate solution to a pH ≥8, and stored in pair A of the large storage tanks. About 1,750 gallons of neutralized metal waste plus coating solution must be stored each day in these tanks if the extraction precipitation is carried out in 20% UNH solution and one-third ton per day of metal is processed.

For neutralization, in either process, the metal waste solution is pumped into the carbonate solution slowly and with good stirring. Although this requires more alkali than if the carbonate were added to the metal .

waste (because the carbonate is reacted partly to bicarbonate instead of to CO_2), it minimizes CO_2 evolution and therefore the danger of foaming over during neutralization. Also, when the waste solution is added to the carbonate no precipitate forms, whereas adding carbonate to the waste forms a voluminous precipitate which then redissolves in excess carbonate. This precipitation is of no great consequence, however, for the precipitate dissolves very rapidly on the addition of excess carbonate. Plant experience may show that the foaming from vigorous CO_2 liberation in the waste neutralizer is not dangerous, in which case the carbonate may then be added to the metal waste, with consequent saving in alkali and in the volume of neutralized waste that must be stored. The possible savings may be estimated from the figures in Table I in the Appendix, which show the alkali consumptions for particular waste metal solutions for the two modes of neutralization.

Neutralized metal wastes from the bismuth phosphate and from the wet fluoride processes can be mixed in any proportion without precipitation, provided the pH of each is >8. The same pair of large waste storage tanks are therefore used for the metal wastes from either process.

C. By-Product Precipitate Solutions

The $BiPO_4$ by-product precipitate solutions are neutralized with excess 30% sodium carbonate solution and stored in pair B of the large underground tanks (decontamination waste tanks). About 270 gallons of neutralized slurry containing from 5-10% of the fission activity must be stored each day.

In the case of fluoride by-product precipitates, the more active ones are dissolved out with Zr solution, while the less active ones are merely slurried out with water. In either case, Na_2CO_3 is used for neutralizing and the resulting slurry is also stored in pair B. At present no provision is made for keeping the by-product slurries separate in order to make them available for experimental purposes. If this is desired, these slurries can be stored in one of the 44,000 gallon buried tanks used now as spares.

D. Active Decontamination Waste

Waste solution from the first decontamination cycle is too active to be disposed of directly to the river. Assuming ten percent of the by-product activity to be in the decontamination waste solution, it would require 5,000 gallons per minute of inactive water over a 24-hour period to dilute one batch of decontamination waste solution to the level of 1×10^{-4} curies/cu.ft., or 2×10^{-11} watts/cc., equivalent to a radiation intensity of 0.1 r./24-hours within the solution (see Appendix). Since the facilities at Clinton are not adequate at present to handle this amount of dilution water, it is intended that the decontamination waste and by-product solutions be neutralized to pH >7 and stored in the large underground tanks to allow part of the activity to decay, thereafter requiring less dilution water for safe disposal into the river. Either NaOH or Na_2CO_3 is satisfactory for neutralizing decontamination wastes from either the $BiPO_4$ or the

wet fluoride process. Since there are facilities for only one alkali, and Na_2CO_3 must be used for neutralization of the metal-containing wastes, Na_2CO_3 will be used for the decontamination wastes also. Again, the waste solution must be pumped into the carbonate solution to minimize CO_2 evolution and foaming, unless plant experience shows the reverse procedure is safe, in which case a saving in carbonate and in volume of stored waste would result (see Table I, Appendix).

For the $BiPO_4$ process, one pair of these large storage tanks would hold about 150 days' output of neutralized decontamination waste (for the wet fluoride, several years' output). The decontamination waste storage capacity of the existing tanks may be extended indefinitely, with minimum dilution water requirement, by storing the neutralized decontamination wastes in the remaining four large underground tanks until all but one are filled, and thereafter pumping the longest-stored tankful into the river with the required amount of dilution water, while the remaining empty tank is filling up. In this way the minimum hold-up of decontamination waste in the tanks would be 225 days, during which time the activity would decay about twenty-fold, thus requiring twenty-fold less dilution water than if diluted and discarded without prior storage, i.e., 250 instead of 5,000 gallons per minute. If only three of the large tanks were used in this storage and dilution cycle, the minimum hold-up of decontamination waste would be 150 days, resulting in approximately a ten-fold reduction in activity and in dilution water required. With only two tanks, 75 days minimum hold-up, with about five-fold reduction in activity and dilution water, would be required.

E. Concentration Waste

The non-metal-containing concentration waste is neutralized and stored temporarily in the small underground storage tanks. For the $BiPO_4$ process, about 2100 gallons of neutralized waste plus by-product precipitate solution are stored per day. Since the activity should be less than 1/2% of the original fission activity, these wastes can be diluted and sent to the river via the large retention pond with correspondingly less than 250 g.p.m. of inactive water. Should the activity be higher than anticipated, these wastes can be added to the decontamination wastes in the large tanks for activity decay.

F. Room D Wastes

These wastes, amounting to 500 gallons every other day (double batches are processed in room D), contain more equivalents of alkali than of acid, so neutralization is not necessary. The composite room D waste is handled in the same manner as the neutralized concentration wastes (E).

G. Inactive Process Water

The inactive process water, along with floor washings, etc., is sent to one of two 22,500 gallon retention ponds. Active wastes may be

pumped into this stream for dilution and discharge. Here the wastes are monitored to make sure that the activity is below the tolerance limit of 1×10^{-4} curies per cu.ft. before discharging into the river. The amount of this inactive water is estimated to be 200-400 g.p.m., which may be adequate for dilution of the concentration wastes plus the decayed decontamination waste.

IV. Process Variables

A. Addition of Reagents

The sodium carbonate is added to the neutralization tank first for two reasons:

1. This order of addition gives much less foaming than the reverse, due to the formation of bicarbonate rather than CO_2. Experimental data indicate that addition of reagents in this order gives about half as much CO_2 as addition in the reverse order.

2. In this method the metal carbonate complex forms immediately and it is not necessary to go through an intermediate precipitate stage.

B. Agitation

It is recommended that solutions in the neutralization tank be agitated vigorously during neutralization to decrease CO_2 formation and to reduce foaming.

Provision should be made for air agitation in all storage tanks, since it is desirable that solids be suspended during pumping operations.

C. Temperature

The 30% sodium carbonate solution should be maintained at 30-40° C. to keep the carbonate in solution. If all solutions are neutralized at about 35° C., the temperatures of the neutralized slurries should not rise to more than 60° C., due to heat of neutralization.

NEUTRALIZATION STEPS

Material	TOTALS	H2O (18)	HNO3 (63)	H3PO4 (98)	H2SO4 (98)	UO2(NO3)2·6H2O (502)	Fe(NH4)2(SO4)2·6H2O (392)	Al(NO3)3 (213)
	Mol.Wt.							
(1) ALUMINUM COATING NEUTRALIZATION								
Aluminum Coating Solution and Acid Rinse	1,345 # / 156 Gal.	1256./92.7	24./1.8			2./0.1		63./4.7
Sodium Carbonate Solution	518 # / 47 Gal.	363./70.						
Neutralized Coating Slurry	1,863 # / 203 Gal.	1620./86.6				(2.)/0.1		(63.)/3.4
(2) METAL WASTE SOLUTION								
Metal Waste Solution and Washes	7,815 # / 765 Gal.	5588./71.5	58./0.7	474./6.1	283./3.6	1412./18.1		
Sodium Carbonate Solution	8,420 # / 765 Gal.	5894./70.						
Neutralized Metal Waste Slurry	16,235 # / 1,530 Gal.	11577./71.3				(1412.)/8.7		
(3) FIRST BiPO4 BY-PRODUCT NEUTRALIZATION								
First BiPO4 By-Product Solution	1,000 # / 90 Gal.	503./50.3	473./47.3					
Sodium Carbonate Solution	1,800 # / 180 Gal.	1260./70.						
Neutralized By-Product Slurry	2,800 # / 270 Gal.	1815./64.9						
(4) DECONTAMINATION WASTE NEUTRALIZATION								
Decontamination Waste Solution and Washes	10,846 # / 1,217 Gal.	9630./88.8	554./5.1	554./5.1			(103.)/1.0	
Sodium Carbonate Solution	8,290 # / 754 Gal.	5803./70.						
Neutralized Decontamination Waste Slurry	19,136 # / 1,971 Gal.	15548./81.3						
(5) SECOND BiPO4 BY-PRODUCT NEUTRALIZATION								
Second BiPO4 By-Product Solution	1,000 # / 90 Gal.	503./50.3	473./47.3				(103.)/0.5	
Sodium Carbonate Solution	1,800 # / 180 Gal.	1260./70.						
Neutralized By-Product Slurry	2,800 # / 270 Gal.	1815./64.9						
(6) CONCENTRATION WASTE SOLUTION								
Concentration Waste Solution	11,029 # / 1,282 Gal.	10173./92.2	482./4.4	79./0.7				
Sodium Carbonate Solution	5,700 # / 520 Gal.	4000./70.						

For steps 6 and 7 the four right-hand columns are re-labelled:

Material	TOTALS	H2O (18)			KOH (56)	KP (58)	KNO3 (101)	LaF3 (196)
Neutralized Concentration Slurry	16,729 # / 1,802 Gal.	14264./85.3			50./1.2	40./0.9	130./3.0	(7.)/0.2
(7) ROOM D WASTE COMPOSITE								
Room D Waste Composite	4,244 # / 500 Gal.	4000./94.3			50./1.2	40./0.9	130./3.0	(7.)/0.2
Room D Waste Slurry	4,244 # / 500 Gal.	4000./94.3			50./1.2	40./0.9	130./3.0	(7.)/0.2

CONDITIONS AND REMARKS

1. Aluminum Coating Neutralization
Temperature: 35-40°C. Waste solution added to the carbonate (instead of carbonate to waste) to prevent excessive CO2 evolution. Carbonate make-up tank kept at 35-40°C. to keep carbonate in solution. Temperature rise from neutralization not more than 20°C. Agitation while neutralizing sufficient to keep solids suspended. Send to large storage tank A (50' x 12').

2. Metal Waste Neutralization
Same as step (1). Send neutralized slurry to large storage tank A.

3. First BiPO4 By-Product Neutralization
Same as step (1). Neutralize and send to large storage tank B.

4. Decontamination Waste Neutralization
Neutralize as in step (1). Send to large storage tank B.

5. Second BiPO4 By-Product Neutralization
Neutralize as in step (1). Send to large storage tank B.

Concentration by Wet Fluoride Process

6. Concentration Waste Neutralization
Neutralize as in step (1). Send to small storage tank for temporary storage.

7. Room D Waste Composite (Basis: 1340 lbs. of metal, every other day)
Composite is alkaline. Send to small storage tank as in step (6).

→ To small storage tanks (2052 gallons per day to temporary storage)

Hg(NO₃)₂ 1½ H₂O 324	La(NO₃)₃ 2NH₄NO₃ 4H₂O 529	NaBiO₃ 280	BiPO₄ 304	HF 20	H₂O₂ 34	Na₂CO₃ 106	NaHCO₃ 84	NaNO₃ 85	Na₃PO₄ 164	Na₂SO₄ 142	NaF 42	CO₂ EVOLVED 44	EXPERIMENTAL DATA GAL. 30% Na₂CO₃/GAL. WASTE	APPROXIMATE DISTRIBUTION OF FISSION ACTIVITY	DENSITY AT 25°C. (g./cc.)	FREEZING POINT (°C.)
0.5 / 0.04	9 lbs. NO evolved 108 c.f. at S.T.P.														1.036	-3
						155. / 30.							0.3		1.327	30
0.5 / —						(123.) / 6.6	20. / 1.1	32. / 1.7				(3) / 25 c.f.		0.2%	1.055	-3.5
						2526. / 30.							1.0		1.241	-5.8
						540. / 30.									1.327	30
		4.5 / 0.4	(20.) / 2.0			(811.) / 5.2	890. / 5.5	78. / 0.5	793. / 4.9	410. / 2.5		(234) / 1910 c.f.	2.0	90.0%	1.291	-5.9
						540. / 30.									1.34	-18
															1.327	30
		(4.5) / 0.1	20. / 0.7			54. / 1.9	140. / 5.0	638. / 22.8				(129) / 1050 c.f.		5.0%	1.186	-13
						2487. / 30.							0.62		1.046	-50
		4.5 / 0.4	(20.) / 2.0			440. / 2.3	1081. / 5.7	748. / 3.9	928. / 4.8			(283) / 2320 c.f.		5.0%	1.071	-3.2
						540. / 30.							2.0		1.34	-18
															1.327	30
	6. / 0.05	(4.5) / 0.1	20. / 0.7	200. / 1.8	(89.) / 0.8	54. / 1.9	140. / 5.0	638. / 22.8				(129) / 1050 c.f.		0.5%	1.186	-13
						1700. / 30.							0.4		1.034	-7.0
															1.327	30
Na₂Cr₂O₇ 262	6. / —				(89.) / 0.5	103. / 0.6	845. / 5.1	690. / 3.9	132. / 0.8		420. / 2.5	(220) / 1800 c.f.		0.5%	1.084	-6.5
(4.) / 0.1	(1.) / —				(12.) / 0.3										1.033	-2.5
(4.) / 0.1	(1.) / —				(12.) / 0.3									0.5%	1.033	-2.5

APPENDIX

Activity of Decontamination Wastes

Assume that 2,000 gallons per day of decontamination waste containing ten percent of the fission activity from one-third ton of metal reacted at 15 kw./ton for thirty days and cooled twenty-five days, are to be diluted so that the intensity of radiation in the waste is not more than 0.1 r./24-hours.

The maximum allowable radiation intensity in the solution is given by

$$I = \frac{4\pi I_o}{\mu} = 0.1 \text{ r./24 hrs.} = 0.033 \text{ r./8 hrs.}$$

where I_o = intensity per cc. solution at 1 cm.

and μ = absorption coefficient in the solution (= 0.05 cm.$^{-1}$).

Therefore $I_o = \frac{(0.033)(0.05)}{4\pi} = 1.31 \times 10^{-4}$ r./8 hrs.

Since 1 watt = 7.5×10^6 r./8 hrs. at 1 cm., $I_o = 1.75 \times 10^{-11}$ watts/cc.

The original fission activity is $1/3 \times 15 = 5$ kw. After the cooling period it is a thousand-fold less, or 5 watts. The fission activity in the decontamination waste is ten percent of this, or 0.5 watt.

The total volume of diluted waste should therefore be at least

$$\frac{0.5}{1.75 \times 10^{-11}} = 2.86 \times 10^{10} \text{ cc.}$$

$$= 7.5 \times 10^6 \text{ gallons}$$

$$= 5 \times 10^3 \text{ gallons/minute for 24 hours}$$

Effect of Mixing Wet Fluoride and Bismuth Phosphate Metal Wastes

No additional precipitate is formed by mixing wet fluoride and $BiPO_4$ metal wastes if the pH of each is kept at or above 8. When the pH drops much below 8, a heavy yellow precipitate forms.

TABLE I
RELATIVE AMOUNTS OF CARBONATE REQUIRED FOR NEUTRALIZATION OF BISMUTH PHOSPHATE AND WET FLUORIDE SEMI-WORKS METAL WASTES

Type Waste	Method of Neutralization	Volume 30% Na_2CO_3 Required per 100 Volumes Waste			
		pH 7	pH 8	pH 9	pH 10
BiPO$_4$ Metal Waste	CO_3 to Waste	51	54	65	122
" " "	Waste to CO_3	83	96	119	---
Wet F " "	CO_3 to Waste	36	44	53	77
" " "	Waste to CO_3	56	60	71	---

This table also shows the quantity of carbonate required to change the mixtures from one pH to another. The differences in alkali required with the method of mixing are due to the difference in proportions of HCO_3^- and CO_2 formed.

TABLE II
VOLUME OF ALKALI REQUIRED PER VOLUME OF WASTE

Waste	Alkali	Gal. Waste per Gal. Alkali	Gal. Alkali per Gal. Waste
BiPO$_4$ Metal	30% Na_2CO_3	1.0	1.0
" "	30% NaOH	3.4	.29
" "	50% NaOH	5.6	.18
Wet F "	30% Na_2CO_3	1.5	.67
" "	30% NaOH	5.4	.19
" "	50% NaOH	9.5	.11
BiPO$_4$ By-Product Solution in 10N HNO_3	30% Na_2CO_3	0.5	2.0
"	30% NaOH	0.9	1.1
BiPO$_4$ Decontamination	30% Na_2CO_3	1.6	.62
" "	50% NaOH	3.3	.26

All values in this table are figured on a ten percent excess by volume of alkali required to neutralize to pH 7.

TABLE III
PERCENT SOLIDS BY WEIGHT OF WASTES NEUTRALIZED WITH 30% Na_2CO_3

Waste	pH	% Wet Solids	% Dry Solids
Aluminum Coating	7	38	7
" "	9	30	7
" "	10	18	7
$BiPO_4$ Metal Solution	7	29	26
" " "	8	none	--
Wet F " "	7	none	--
$BiPO_4$ Decontamination	7	7	3

The percent of wet solids was obtained by centrifuging for 15 minutes at 3000 r.p.m. Dry solids were obtained by drying the wet precipitate at 70° C. for twenty hours for the aluminum coating solutions, and two hours for the others.

The wet fluoride metal waste solution used had been reduced with H_2O_2.